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PATENT SPECIFICATION

NO DRAWINGS

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Inventor: MANUEL ALBERT JORDAN

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COMPLETE SPECIFICATION

Compositions containing Crotonaldehyde Resins

We, SCHENECTADY CHEMICALS INC., a Corporation organized and existing under the laws of the State of New York, New York, United States of America of Schenectady 1, New York, United States of America, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions containing crotonaldehyde resins and more particularly to compositions which comprises a rubbery polymeric substance and, as a tackifier therefor, a crotonaldehyde resin.

The most frequently used tackifier for the well known SBR rubber (rubbery butadiene-styrene copolymer) is a material known as Koresin which is a reaction product of p-tertiary butyl phenol and acetylene. The tack properties imparted to SBR rubber by means of this compound tend however to deteriorate with age. It is an object of the present invention to provide new compositions having a basis of rubbery polymeric substance and containing a tackifying agent which imparts tack properties of improved permanence.

According to the present invention there is provided a composition comprising a rubbery polymeric substance and, as tackifier therefor, a resin obtained by reacting an aldehyde component consisting predominantly of crotonaldehyde with a phenolic component consisting predominantly of a nuclear alkyl substituent phenol (monohydroxybenzene) in which the alkyl substituent contains at least 4 carbon atoms, and/or a dihydroxybenzene.

Of the aforesaid resins those derived from nulear alkyl substituted phenols are preferred and, within that class, those in which the alkyl substituent contains 8 to 12 carbon atoms. The most preferred phenolic reactant is dodecyl phenol.

The phenolic reactant may, however, include other phenols in less than major proportion, e.g. it may contain less than 50 mole per cent of phenol or cresol. The phenolic reactant may be or include a mixture of the higher alkyl phenols referred to or a mixture of one or more higher alkyl phenols with one or more dihydroxybenzenes.

Examples of suitable alkyl phenols are p-octyl phenol, p-decyl phenol, p-dodecyl phenol, p-octadecyl phenol, p-tertiary butyl phenol, p-sec. amyl phenol, p-isooctyl phenol, o-dodecyl phenol, o-butyl phenol, o-octyl phenol, m-hexyl phenol, m-octyl phenol, m-dodecyl phenol, p-isodecyl phenol.

As dihydric phenols there can be employed resorcinol and hydroquinone.

The aldehyde reactant is preferably crotonaldehyde itself (i.e. as the sole reactant) but it may contain other reactive aldehydes, e.g. up to 50 mole per cent of formaldehyde.

The reaction is preferably effected using a ratio of 0.3 to 2 moles of total aldehyde per mole of total phenolic reactant. The reaction is preferably carried out in the presence of an acid catalyst though alkaline catalysts e.g. sodium hydroxide may alternatively be employed.

The following is a typical general procedure for making a crotonaldehyde-alkyl phenol resin for use in the present invention: The phenol composition is charged in a 3-neck flask having a thermometer, stirrer and reflux condenser. The catalyst, e.g. sulfuric acid or aqueous oxalic acid, is added and the flask heated to 190°F. at which point the crotonaldehyde (alone or admixed with aqueous formaldehyde) is added very slowly. A slight exothermic reaction occurs. The mixture is refluxed for 2 to 4 hours at 205—215°F. and is then distilled under vacuum until most of the unreacted volatiles are removed and the temperature of the resin has reached 265—280°F.

The resins obtained vary in physical character from liquid tacky products to semi

[*Price*

solids and solids having melting points well above room temperature.

The following procedures will serve to illustrate the production of suitable crotonaldehyde resins for use in the invention. In these procedures, as elsewhere in this specification unless otherwise stated, the parts and percentages given are by weight.

RESIN I

p-octyl phenol	1030 grams (5 moles)
15% aqueous hydrochloric acid	11 grams
crotonaldehyde (89%)	394 grams (5 moles)

The resin produced using the procedure just described was a semi solid.

The crotonaldehyde used in the example (and all of the other examples showing the preparation of resins) was 89% crotonaldehyde, the balance being water. Thus of the 394 grams of 89% crotonaldehyde used in this example 350 grams (or 5 moles) was crotonaldehyde.

RESIN 2

p-octyl phenol	1030 grams (5 moles)
oxalic acid } solution	34 grams
water } solution	100 grams
crotonaldehyde (89%)	197 grams (2.5 moles)
formaldehyde (37%)	162 grams (2.5 moles)

The resin produced by the general procedure described above was a heavy, sticky liquid.

RESIN 3

p-octyl phenol	1030 grams (5 moles)
concentrated sulfuric acid	16 grams
crotonaldehyde (89%)	394 grams (5 moles)

The resin produced by the outlined procedure had a melting point of 80—85° C.

RESIN 4

p-octyl phenol	515 grams (2.5 moles)
methane sulfonic acid (70% aqueous solution)	8 grams
crotonaldehyde (89%)	197 grams (2.5 moles)

The resin produced by the above-outlined procedure was a sticky liquid.

RESIN 5

resorcinol	330 grams (3 moles)
oxalic acid } solution	10 grams
water } solution	10 grams
crotonaldehyde (89%)	118 grams (1.5 moles)

The resin produced by the procedure set forth above was a semi solid.

RESIN 6

resorcinol	385 grams (3.5 moles)
phenol	94 grams (1 mole)
oxalic acid } solution	5 grams
water } solution	30 grams
crotonaldehyde	118 grams (1.5 moles)

The resin prepared by using the procedure set forth above saw a sticky liquid.

RESIN 7

p-dodecyl phenol	524 grams (2 moles)
concentrated sulfuric acid	8.5 grams
crotonaldehyde (89%)	130 grams (1.65 moles)

The resin prepared by using the procedure set forth above was a solid having a melting point of 50° C.

The crotonaldehyde resins preferred as described above are of general value as tackifiers for rubbery polymers. They are of especial value as tackifying agents for any of the conventional rubbery butadiene-styrene copolymers. Normally these copolymers contain 25—40% styrene with the balance being butadiene. SBR rubber type 1502 contains 25% styrene and 75% butadiene. The crotonaldehyde resins of the present invention are also useful in tackifying EPT rubbers. These rubbers are terpolymers of ethylene, propylene, and a nonconjugated polyolefin. Thus there can be used 20—80% ethylene, 80—20% propylene and 0.1—10% of the nonconjugated polyolefin in making the terpolymer. Examples of nonconjugated polyolefins are dicyclopentadiene, dicycloheptadiene, pentadiene-1,4 and allo-ocimene. Normally the terpolymer contains 50—60% ethylene, 3—5% of the diene and the balance propylene. Specific examples of such terpolymers are the terpolymer of 60% ethylene, 39% propylene and 1% dicyclopentadiene and the terpolymer of 55% ethylene, 42% propylene and 3% dicyclopentadiene.

In the production of the compositions of the present invention the crotonaldehyde resin is blended with the rubbery polymer by any conventional method, e.g. in a blending mill. Normally 3 to 20 parts of the resin are employed per 100 parts of SBR rubber. Conventional SBR rubber additives, such as sulfur and other vulcanizing agents, antioxidants, accelerators and softening agents, can be incorporated in the composition.

The compositions of the present invention may also be employed as liquid splicing cements. In such case the crotonaldehyde resin may be 5 to 70 parts per 100 parts of rubber, preferably SBR. The non-volatiles normally are not over 50% of the total cement, usually 20—25%. The liquid splicing cement is made by adding a solvent to the crotonaldehyde resin —SBR rubber mixture. The preferred solvents are hydrocarbons, e.g. an equal mixture of toluene and naphtha, although other solvents can be employed.

The following Examples will serve to illustrate the invention:

Example 1

The following formulation was prepared using different resin constituents:—

SBR rubber, type 1502	100 parts
HAF (carbon black)	50 parts
zinc oxide	3 parts
stearic acid	2 parts
diphenyl guanidine (accelerator)	0.3 part
Zalba (a hindered phenol-antioxidant)	1.5 parts
Santocure (N-cyclo-2-benzothiazyl-sulfonamide-accelerator)	1.2 parts
sulfur	2 parts
Circosol ZxH (high molecular weight naphthenic hydrocarbons)	8 parts
resin	8 parts

(Circosol ZxH is a conventional softener and plasticizer for SBR rubber).
(The word Santocure is a Registered Trade Mark).

After the formulations were prepared and milled they were tested for tack properties. Two examples according to the invention were tested and compared with the commercial Koresin tackifier as indicated.

Resin	Tack quality after:		
	24 hours	48 hours	5 days
Koresin	very good	good	fair (50%)
Resin 3	very good	good	fair (50%)
Resin 7	very good	very good	very good (100%)

The physical properties of the formulations were also determined at optimum cure with the following results.

Property	Koresin	Resin 3	Resin 7
Tensile, psi.	2836	2565	3305
Elongation at break (%)	460	480	470
300% Modulus, psi.	1395	1183	1430
Hardness (Shore A)	60	57	60
Cure (298° C.), min.	45	30	30

It can be seen from the results set forth above that Resin 7 was superior to the commercial tackifier, Koresin, in the SBR rubber formulation.

EXAMPLE 2.

A liquid splicing cement was made by adding 20 parts of the formulation of Example 1, using Resin 7 to 80 parts of an equal mixture of toluene and naphtha.

EXAMPLE 3.

Improved tack in the EPT rubber was obtained by mixing 100 parts of a terpolymer of 55% ethylene, 42% propylene and 3% dicyclopentadiene with 8 parts of Resin 7.

WHAT WE CLAIM IS:—

1. A composition comprising a rubbery polymeric substance and, as tackifier therefor, a resin obtained by reacting an aldehyde component consisting predominantly of crotonaldehyde with a phenolic component consisting predominantly of a nuclear-alkyl-substituted phenol in which the alkyl substituent contains at least 4 carbon atoms and/or a dihydroxybenzene.

2. A composition according to claim 1 wherein the resin is one obtained using crotonaldehyde as the sole aldehyde component.

3. A composition according to claim 1 wherein the resin is one obtained using an aldehyde component comprising crotonaldehyde and formaldehyde, the crotonaldehyde constituting at least 50 mole percent of the aldehyde.

4. A composition according to any of claims 1—3 wherein the phenolic component consists predominantly of a nuclear-alkyl-substituted phenol in which the alkyl substituent contains 8 to 12 carbon atoms.

5. A composition according to claim 1 wherein the tackifier is a crotonaldehyde/dodecylphenol resin.

6. A composition according to any of claims 1—5 wherein the rubbery polymer is an SBR rubber.

7. A composition according to any of claims 1—5 wherein the rubbery polymer is an ethylene - propylene - nonconjugated polyolefin terpolymer.

8. A composition according to any of the preceding claims wherein the tackifier is present in a proportion of 3 to 20 parts per 100 parts by weight of the polymer.

9. A composition according to any of the preceding claims in which the specified polymer and tackifier are dissolved in a solvent medium.

10. A composition according to claim 9 wherein the solvent medium is a hydrocarbon solvent medium.

11. A composition according to any of the preceding claims wherein the tackifier is any

one of the Resins 1—7 hereinbefore specifically described.

12. A composition according to claim 1 substantially as hereinbefore described with reference to any of the foregoing specific examples 1 to 3.

Agents for the Applicants,
V. GALLAFENT & CO.,
Chartered Patent Agents,
8 Staple Inn,
London, W.C.1.

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